



Dry autothermal reforming from biomass derived gas under excess enthalpy with porous medium

Ming-Pin Lai ^a, Wei-Hsiang Lai ^{a,b}, Rong-Fang Horng ^{c,*}

^a Department of Aeronautics and Astronautics, National Cheng Kung University, No.1, University Road, Tainan City 701, Taiwan

^b Research Center for Energy Technology and Strategy, National Cheng Kung University, No.1, University Road, Tainan City 701, Taiwan

^c Department of Mechanical Engineering, Clean Energy Center, Kun Shan University, No. 949, Da-Wan Road, Yung-Kang District, Tainan City 710, Taiwan

HIGHLIGHTS

- ▶ A design to preheat and premix the reactants with porous medium in the reforming process.
- ▶ Biomass derived gas is used for reforming for SOFCs and MCFCs.
- ▶ Excess enthalpy is achieved by internal heat recirculation with porous medium installed in the front of reactor.
- ▶ The improvement in reforming efficiency is 33.9% with the CO₂/CH₄ of 1.0 and O₂/CH₄ of 0.75 by using an OBSiC porous medium.

ARTICLE INFO

Article history:

Received 9 March 2012

Received in revised form

31 May 2012

Accepted 3 June 2012

Available online 9 June 2012

Keywords:

Carbon dioxide

Dry autothermal reforming

Hydrogen-rich syngas

Porous media

Excess enthalpy

ABSTRACT

Dry autothermal reforming (DATR) from biomass derived gas (BDG) under excess enthalpy with porous medium (PM) is investigated in this study. Preheating reactant by internal heat recirculation of a PM may enhance the reaction of input mixture and improve production of H₂-rich syngas. Temperature distribution of catalyst and fuel conversion efficiency are studied with various feeding rates of reactant and PM under high-temperature and carbon-rich conditions. Fuel conversion and H₂-rich syngas selectivity are improved by reactant preheating with increased enthalpy of reactant by the heat transfer stored in PM. Control parameters include methane feeding rate, CO₂/CH₄ and O₂/CH₄ molar ratios, and PM material. Experimental results indicate that reformat gas temperature with PM-assisted dry autothermal reforming is higher than the equilibrium adiabatic temperature. The results are helpful to understand the internal heat recirculation under excess enthalpy reaction. In the reforming, it not only provides the required energy for a self-sustaining reaction, but also enhances fuel conversion efficiency. The improvements in methane conversion efficiency is 18%, energy loss percentage 20.7%, and reforming efficiency 33.9%, respectively with the best parameter settings by an OBSiC PM. Additionally, the theoretical production is calculated by the HSC Chemistry software (ChemSW Software, Inc.).

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

CO₂ is the main source of greenhouse gases. The strategy of CO₂ mitigation includes reduction, recycling, reusing, and storage. Among them, CO₂ reduction is the most beneficial method, which is achieved using low-carbon fuels and alternative energy. Biomass-derived gas (BDG) is not only a low-carbon fuel, but also a valuable source of alternative energy. Recently published papers related to energy policy and sustainable energy indicated that several countries are promoting low-carbon energy from BDG [1,2].

BDG is mainly made from biogas, landfill gas, digester gas, and flue gas. The gas composition is complex and variable. BDG would be a promising source of alternative energy if properly managed. If BDG is combusted directly, the methane mixed with carbon dioxide would proportionally decrease the laminar flame speed and adiabatic flame temperature with a high concentration of CO₂. In contrast, if BDG is converted into H₂-rich syngas by a reforming process, the adiabatic flame temperature would be elevated with high CO concentration, and laminar flame speed would be increased substantially with high H₂ concentration in the syngas [3]. Thus, carbon sources from greenhouse gases can be used to produce hydrogen-rich gas fuels. It not only has advantages in fuel economy, but also has essential benefits in CO₂ reduction. Moreover, syngas has various applications, such as co-fire for internal

* Corresponding author. Fax: +886 6 2050509.

E-mail address: hong.rf@msa.hinet.net (R.-F. Horng).

combustion engines [4,5] and combustors, fuel for high-temperature fuel cells (such as SOFC and MCFC) [6], and synthesis of liquid fuels [7] or high-value chemicals [8].

Dry reforming is a suitable approach for BDG fuel processing to produce hydrogen. Fisher and Tropsch initiated the investigation on dry reforming by methane with CO₂ [9]. However, it is a high-temperature and carbon-rich reaction. The deactivation of catalysts caused by sintering and coking inhibited commercial development. Related studies in dry reforming are increasing worldwide because of the advantages dry reforming offers, and increasing greenhouse problems. In recent years, catalyst selection has experienced preliminary progress in dry reforming, including the catalyst material [10], washcoat material [11,12], surface analysis technology, decoking ability [13], the mechanism of carbon formation on catalysts [14], and catalyst preparation methods. In the catalyst material, noble metal catalysts are more suitable for dry reforming reactions than others because of the high activity and the ability of carbon resistance. Ashcroft et al. [10] investigated the catalyst activity and carbon formation in dry reforming with several catalysts, and proposed the active level in descending order, as follows: Ir > Rh > Ni > Pd > Ru, and the carbon deposition level in descending order, as follows: Ni > Pd > Rh ≈ Ru ≈ Ir. Hou et al. [13] indicated that noble metal catalysts (Pt, Ru, Rh, Ir) have a higher carbon resistance ability than Ni and Co catalysts. Although the catalytic activity of Ni competes with those of precious metals, it exhibits carbon deposition in the reforming process. However, use of the Rh catalyst as a promoter verified the improvement in Ni reducibility, which may prevent carbon deposits on the catalyst and also enhance the activity of the catalyst. Alkaline earth metal oxide catalysts were confirmed to have excellent conversion characteristics and high stability. Ruckenstein et al. [11] found that the NiO/MgO catalyst was less likely to cause a CO disproportionation reaction by using a temperature programmed desorption –CO test. Horiuchi et al. [12] indicated that the catalyst may inhibit carbon deposition by alkaline earth metal addition because it may reduce the dehydrogenation of methane by the Ni catalyst.

Carbon formation on the catalyst surface may be prevented by oxygen addition. However, due to effect of strong metal-support interaction (SMSI), the extensive catalyst (Pt) sintering occurred when the sample was pre-treated in an oxidizing environment. Therefore, the excessive amount of oxygen affects catalyst (Pt) dispersion, thereby affecting the activity of the catalyst [15]. Furthermore, the oxidant and reactants should be mixed uniformly; otherwise, it may have a strong oxidation reaction in the catalyst upstream, and cause the problem of catalyst sintering. It would also cause the problem of carbon deposition under carbon-rich conditions in catalyst downstream [16].

Dry reforming is a carbon-rich and endothermic reaction. In addition, the molecule of carbon dioxide is a double-bond structure; therefore, bond breaking is difficult. It must provide external heating or oxygen addition to supply the required energy for reaction; otherwise, the active sites of the catalyst would be sintered and aggregated when temperature distribution is inhomogeneous. In the previous study, combustion efficiency was improved by preheating the inlet fuel mixture [17]. In general, the preheating methods may be divided into two types; that is, including internal preheating and external preheating. For external preheating, a heat exchanger is used for heat transfer by thermal conduction. However, this method has the disadvantage of equipment complexity and operating costs. It is unsuitable for miniaturization application [18]. In the past, the internal preheating method was used to circulate high-temperature exhaust gas back to the combustion zone to increase intake temperature. However, this method may dilute the reactant, thereby limiting the range of reforming reaction.

Fig. 1 shows a concept of internal heat recirculation [19,20]. As shown in the concept schematic diagram, heat loss may cause

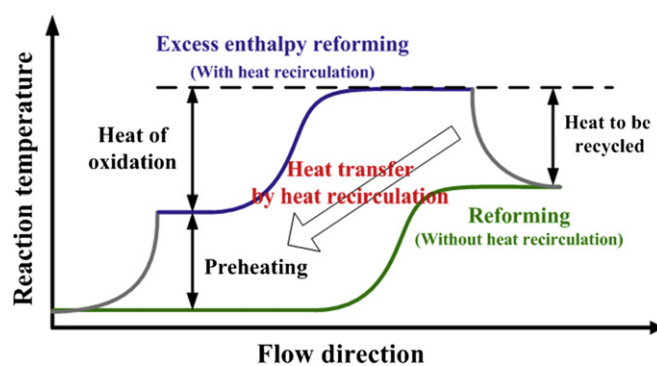


Fig. 1. The heat transfer mechanism by internal heat recirculation (modified after Ref. [20]).

a decrease in catalyst temperature in the reforming process if the reactant is not preheated. Reactant preheating by internal heat recirculation with a porous media may enhance the oxidation reaction, and the temperature may be higher than the adiabatic flame temperature. Consequently, this method not only provided the thermal energy required for a self-sustaining reaction, but also improved fuel conversion efficiency and syngas production. In recent years, several researchers proposed the extension of the flammability limit of premixed flame with porous media burner (PMB) [21–23]. They preheated the reactant species and improved flame stability using internal heat recirculation and flame stabilization mechanism evaluated by the Peclet number [24,25].

Consequently, this study focused on a novel design of porous-catalyst hybrid reactor for dry autothermal reforming. The internal flow of the porous media arrangement in this study differs from that in the combustor and catalytic bed reactor. It combined the benefits of the porous media and catalyst, such as enhancing the preheating reactant by heat recirculation and improving syngas selectivity with the surface reaction of the catalyst. The comparison of porous media and catalyst is listed in Table 1. The porous media adopted in the flow field have several advantages, such as the reactants not being mixed with the products; porous media can be used as a built-in heat exchanger; a wide operating range of flammability limits; and the characteristic of high flame stability. Thus, the heat transfer between gas and solid phases can be enhanced, which is favorable to the mixing effect of the intake species. Thus, this study investigated the effect of excess enthalpy on reforming reaction by using a porous medium to preheat the reactants in the reforming process. This would considerably enhance the reforming reaction and improve H₂-rich syngas production. With these advantages, the reaction chamber may achieve an arrangement with simplification and high energy density by internal heat recirculation.

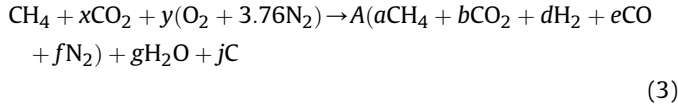
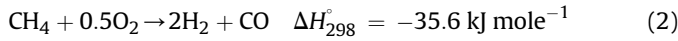
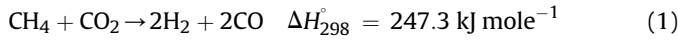
2. Relative calculations

Eqs. (1) and (2) are the theoretical reactions while Eq. (3) is the actual reaction equation. x, y, a, b, d, e, f, g and j are stoichiometric

Table 1
Reactor design and arrangement of fuel converter.

	Porous burner	Reformer	Novel design
Preheating zone	Porous media	N/A	Porous media
Reaction zone	Porous media	Catalyst	Catalyst
Reaction mechanism	Gas phase	Surface	Gas phase + surface
Reaction temperature	>1200 °C	800 °C	<1000 °C
Conversion efficiency	High	Low	High
Syngas selectivity	Low	High	High
Reforming efficiency	Media	Medium	High
Reference	[22,23]	This study	This study (with PM)

factors in the actual reaction, and A is the proportionality constant, respectively.



The energy recirculation can be calculated by Eq. (4) [19]. The equilibrium adiabatic temperature was calculated by Eq. (5).

$$\int_{T_0}^{T_f} mc_p dT = Q_c + Q_a = H_f - H_0 \quad (4)$$

$$\sum_R n_i (\bar{h}_f^0 + \bar{\Delta h})_i = \sum_P n_e (\bar{h}_f^0 + \bar{\Delta h})_e$$

$i = \text{CH}_4, \text{CO}_2, \text{O}_2, \text{N}_2;$
 $e = \text{CH}_4, \text{CO}_2, \text{O}_2, \text{N}_2, \text{H}_2, \text{CO}, \text{H}_2\text{O}, \text{C}$ (5)

In Eq. (4), T_0 and T_f are the initial and final temperatures, respectively; c_p is the constant pressure specific heat; Q_c and Q_a are the heat release from chemical energy conversion and energy added during the reaction, respectively; H_f and H_0 are the enthalpy of reaction and enthalpy of reference, respectively. In Eq. (5), n , \bar{h}_f^0 and $\bar{\Delta h}$ represent the number of kilogram-moles, enthalpy of formation and enthalpy change of species e and i for the products and reactants, respectively.

The energy loss percentage, reforming efficiency and thermal efficiency can be calculated as follows:

$$\text{Energy loss percentage} = \left(\frac{\text{abs}(\Delta H)}{\text{LHV}_{\text{simulated fuel}}} \right) \times 100\% \quad (6)$$

$$\eta_{\text{reforming}} = \frac{\dot{m}_{\text{H}_2} \text{LHV}_{\text{H}_2} + \dot{m}_{\text{CO}} \text{LHV}_{\text{CO}}}{\dot{m}_{\text{simulated fuel}} \text{LHV}_{\text{simulated fuel}}} \times 100\% \quad (7)$$

$$\eta_{\text{thermal}} = \frac{\dot{m}_{\text{H}_2} \text{LHV}_{\text{H}_2} + \dot{m}_{\text{CO}} \text{LHV}_{\text{CO}} + \dot{m}_{\text{CH}_4} \text{LHV}_{\text{CH}_4}}{\dot{m}_{\text{simulated fuel}} \text{LHV}_{\text{simulated fuel}}} \times 100\% \quad (8)$$

where in Eqs. (6)–(8), LHV_{H_2} , LHV_{CO} and $\text{LHV}_{\text{simulated fuel}}$ are the lower heating values of hydrogen, carbon monoxide and simulated BDG, respectively; ΔH represents the change of enthalpy of reaction; and \dot{m}_{H_2} , \dot{m}_{CO} and $\dot{m}_{\text{simulated fuel}}$ are the mass flow rates of hydrogen, carbon monoxide and simulated BDG, respectively.

3. Experimental set-up and method

3.1. Experimental set-up

The experimental apparatus included a reforming unit, reactant supply system, data acquisition system, gas sampling/analyzing system. The schematic of experimental arrangement is shown in Fig. 2. The reforming unit consisted of the reactant nozzle, mixing chamber, preheating zone of porous media, catalyst reaction bed, arc ignition device and products collection zone. In order to enhance the mixing of reactants in the limited space, the reactants were fed into the reaction chamber with a tangential flow to induce the swirling flow. Furthermore, the sudden-expansion design in the mixing chamber was also to enhance the mixing of reactants. The porous medium was installed in the upstream of the catalyst to preheat the reactants by heat recirculation. The geometry of the medium also had the effect to enhance the mixing of intake reactants. The thermo-physical property and the specifications of the porous media are shown in Table 2. The porous media could be divided into two kinds of structures, including ceramic foam and honeycomb. The types of material composition include oxide-bonded silicon carbide (OBSiC), Alumina oxide (Al_2O_3), Zirconia oxide (PSZT), Cordierite and metallic alloy (Fe–Cr–Al). The porosity of ceramic foam structure is ranged from 80 to 85%, such as OBSiC, Al_2O_3 and ZrO_2 , with the pore size of 15 PPI. The honeycomb structures of Cordierite and metallic alloy are both in the cell density of 200 CPSI. In addition, the thickness of PMs is 22 mm in this study.

Because the experiment is for hydrogen production by reforming, pure silicon carbide could cause the oxidation and hydrogenation reactions under high temperature conditions [26], which would affect the media structural stability. Therefore, the silicon carbide with metal oxide was adopted to avoid the oxidation and hydrogenation in this study, and thereby increased the heat capacity of silicon carbide.

The catalyst was a commercialized Pt–Rh/ Al_2O_3 –CeO₂. The weight ratio of Pt/Rh is 5, and catalyst loading amount (g ft^{-3}) is 50. The cells per square inch are about 200, and the diameter of catalyst bed is 46.2 mm. The catalysts made of metallic monolith (Fe–Cr–Al)

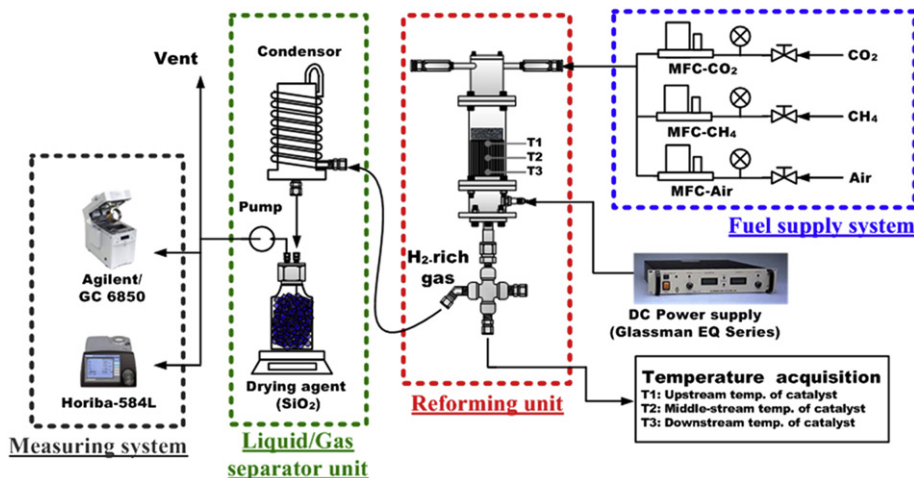


Fig. 2. Schematic of the experimental set-up.

Table 2
Thermo-physical property and specifications of porous media.

Materials	Ceramic foam			Honeycomb	
	OBSC	Al ₂ O ₃	PSZT	Cordierite	Metallic alloy
Composition	45–55%–SiC, 15–20%–Al ₂ O ₃ , 30–35% (3Al ₂ O ₃ –2SiO ₂)	99.5% Al ₂ O ₃	97%–ZrO ₂ , 3%–Mg	MgO–Al ₂ O ₃ –SiO ₂	Fe–Cr–Al
Max. usage temperature, °C	1500	1700	1760	1360	1420
Unit diameter, mm	φ50	φ50	φ50	φ50	φ50
Unit thickness, mm	22	22	22	22	22
Porosity, %	80–85	80–85	80–85	–	–
Pore per inch, PPI	15	15	15	–	–
Cell per square inch, CPSI	–	–	–	200	200
Bulk density, gcm ^{−3}	0.6	0.6~0.79	0.84~1.12	–	–
Heat capacity, Jkg ^{−1} K ^{−1}	670	880	400	–	–
Thermal conductivity, Wm ^{−1} K ^{−1}	77–126	20–40	1.8–2.5	–	–
Thermal shock	23	3	1	–	–



with low pressure drop, high strength and high thermal conductivity are favorable to the transient response and rapid cold starting. Arc generator consisted of spark igniter (NGK CR8EGP) and DC power supply (Glassman EQ series). It was to provide the ignition energy required for initiating the reaction during cold starting. Gas collection zone was used to collect the products for analysis. The reformate gas was cooled to separate the liquid/gas phases by a cooling unit with a fin-and-tube heat exchanger. After cooling process, the residual moisture was absorbed by drying-agent (SiO₂) to prevent the liquid species to pollute or even damage the analyzer. A mass flowmeter (Brooks Instrument Model 5850S, made in USA) was used to determine the feeding rate and molar ratio of the reactants. The catalyst temperature, reactant feeding rate and real-time concentration of products were recorded by a data acquisition system. In order to know the temperature gradient in the autothermal reforming reaction, the reaction temperatures were measured in the upstream, middle-stream and downstream of the catalyst, respectively. A gas chromatographer (Agilent GC-6850) was used for determining the gas species in the products. An emission analyzer (Horiba MEXA-584L) was used for the real time monitoring of the gas emissions, such as CO, CO₂, O₂...etc.

3.2. Experimental method

This study focused on the heat recirculation characteristics of the porous media, which transferred the heat to the reactants in the catalyst upstream and thereby preheated the reactants, so that the intake enthalpy was elevated. Fig. 3 demonstrated the schematic of heat recirculation of porous medium for assisting reforming. The porous medium was installed in the upstream of the catalyst reaction zone. It could be found in the figure that catalytic reaction zone could transfer the heat to porous medium by radiation. Between the catalytic reaction zone and porous medium preheating zone, the heat was transferred by conduction via solid–solid interface; and the heat exchange between the porous medium and the reactants could be enhanced by convection [27]. The porous medium is an inert substance, which is not involved in the chemical reactions. It plays the role of reactant preheating and energy trapping. In this study, in order to achieve the effectiveness of excess enthalpy for reforming, the reactants were preheated by the thermal energy stored in the porous medium from dry autothermal reforming by internal heat recirculation. As shown in the schematic, excess enthalpy can improve the reaction temperature

of catalyst bed in the reforming, and the temperature even higher than the equilibrium adiabatic temperature.

Fig. 4 shows the reaction temperature on the theoretical equilibrium molar yield of products under various CO₂/CH₄ molar ratios calculated via minimization of Gibbs free energy by using HSC Chemistry software package [28]. The products include hydrogen and carbon dioxide (in Fig. 4A), carbon monoxide and water (in Fig. 4B), and carbon and methane (in Fig. 4C). The reaction temperature is between 600–1200 °C. The parameters for dry reforming were set as CO₂/CH₄ = 1 and O₂/CH₄ molar ratio between 0 and 1. It can be found in Fig. 4(A), (B) and (C), when O₂/CH₄ molar ratio is zero, and the high temperature is favorable for carbon dioxide and methane to convert to hydrogen and carbon monoxide. However, the carbon formation is the main disadvantage in the dry reforming. Accordingly, the catalyst might be deactivated due to the carbon deposition on the surface, or even the reforming reaction might be terminated. In order to prevent the carbon formation and

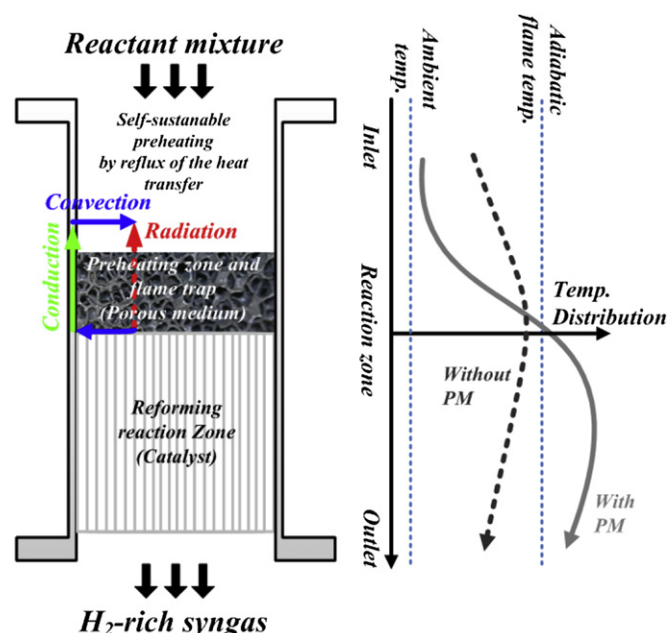


Fig. 3. The heat recirculation mechanism of porous media assisted reforming.

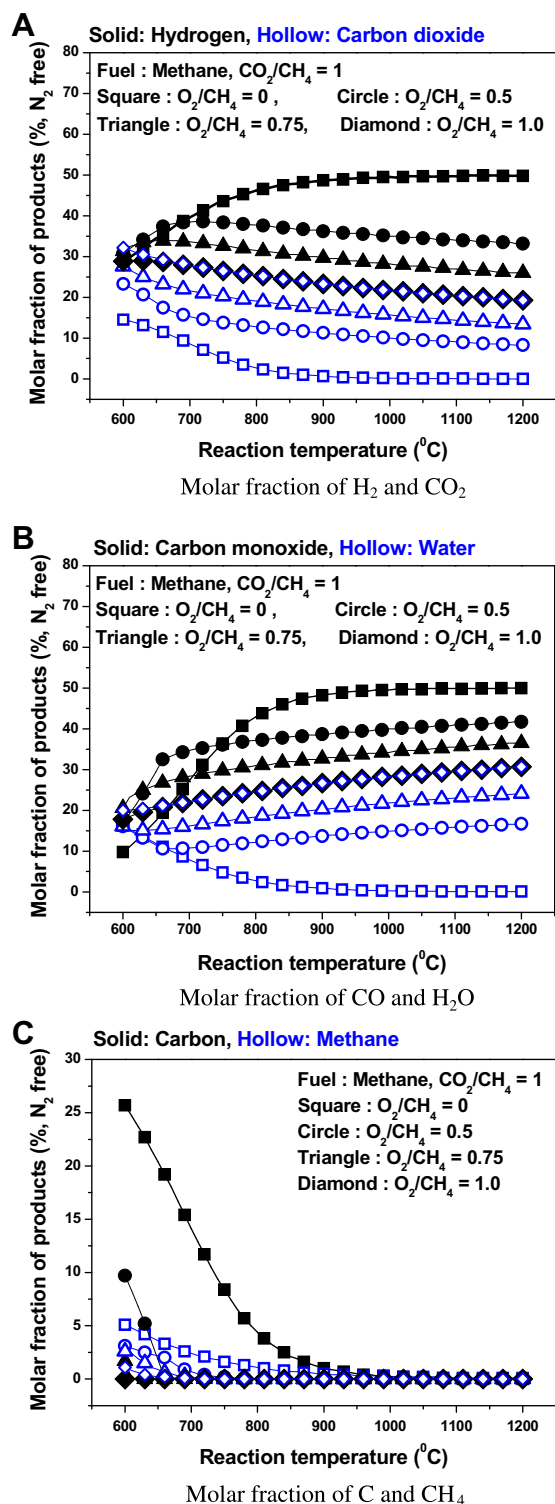


Fig. 4. Effect of reaction temperature on molar fraction of products under different O_2/CH_4 molar ratio.

to increase the fuel conversion and syngas production, appropriate quantity of oxidant can be added for oxidation reaction. Simultaneously, the self-sustaining reaction could be achieved because of the heat release of oxidation in the reforming process. However, excessive oxygen was not allowed. The theoretical chemical equilibrium calculations indicated that the oxidant could react with syngas and thereby reduce the production of hydrogen and carbon

monoxide. Therefore, the dry autothermal reforming reaction has a negative impact of syngas production under the high O_2/C molar ratio.

Consequently, the main composition of biomass derived gas, namely 50–75% CH_4 , 25–50% CO_2 , was used for the reactant species setting in this study. In light of the above, the reforming parameters were set as methane feeding rate 10 NL min^{-1} , the CO_2/CH_4 molar ratio between 0 to 1 and the O_2/CH_4 molar ratio between 0.5 to 1.0. In addition, the selected porous media included OBSiC, Al_2O_3 , ZrO_2 , Cordierite, and Fe–Cr–Al alloy. The effect of reactant feeding ratio on the reforming performance was investigated; and then the excess enthalpy on temperature distribution of catalyst bed with different porous media was explored.

4. Results and discussion

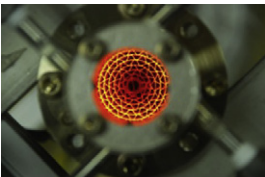
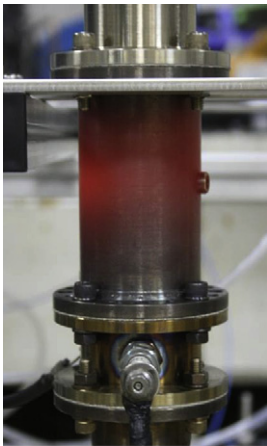

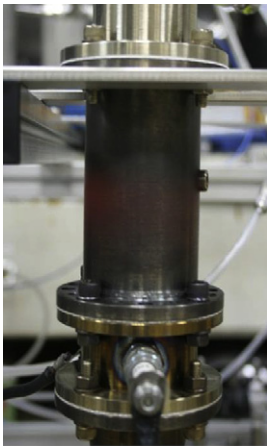
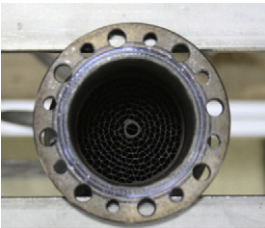

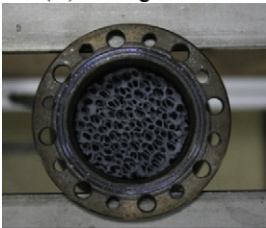

4.1. Effect of excess enthalpy on reaction gas temperature

As can be seen through enthalpy, raising the O_2/CH_4 molar ratio can free up a corresponding heat release of oxidation to provide the energy required for the reforming reaction. Because the activity of the catalyst is dominated by the surface reactions, this study therefore used autothermal reforming to supply the energy necessary for the catalyst surface reaction. The next step is to explore the effect of porous media on the reformat gas temperature in the catalyst reaction zone.

Table 3 shows a comparison of photographic observations of internal flow fields with and without a PM. Each observation is divided into a top view and a side view. The top view displays a schematic diagram that mainly showed any placement of porous media within the internal flow field before the reaction (Table 3(B) and (E)), and any observed fire-color during the reaction (Table 3(A) and (D)). The side view displays the wall heat dissipation of the internal flow field with or without the placement of a porous media (Table 3(C) and (F)). The reforming parameters consist of a methane feed flow rate of 10 NL min^{-1} and an O_2/CH_4 molar ratio of 1, with oxide-bonded silicon carbide as the PM. Temperature data in the table show for those reactions in which a PM was placed, the reformat gas temperature of each position of the catalyst could effectively be raised to 150–200 $^\circ\text{C}$. The fire observation in the side views of Table 3(C) and (F) show that adding PM can effectively reduce wall heat dissipation, which is accomplished mainly by using various heat recirculation mechanisms, such as conduction and convection, which feed the heat stored in the wall back into the PM. Furthermore, by placing a PM inside the flow field, the speed of the gas flow inside the tube and the area of heat exchange have increased correspondingly; strengthening the convection heat transfer effect from the solid to the gaseous interface, thereby preheating the upstream reactants and reducing wall heat loss. In addition, images from Table 3(A) and (D) show that those reactions with a PM in the internal reaction flow field are able to prevent the low temperature fluid from directly entering the catalyst reaction zone, which overcomes the problems of temperature and concentration gradients in the radial of the catalyst. These photographic observations confirm the fact that the porous medium installed in front of the catalyst can stimulate the gas distribution of the flow field and the heat recirculation for the reforming reaction.

Fig. 5 shows the comparison between the equilibrium adiabatic temperature and the measured reformat gas temperature experimentally. The parameters for the methane feed rate was set to 10 NL min^{-1} with an O_2/CH_4 ratio of 0.5–1, where the CO_2/CH_4 ratio was between 0 and 1. Reformat gas temperature was derived from the average value of the inlet, middle and outlet catalyst temperatures. In general, the higher O_2/CH_4 leads to the larger heat release of oxidation, and results in the higher corresponding reformat gas

Table 3
Photographic observation on with or without porous media assisted DATR.

Without PM assisted		With PM (OBSiC_15ppi*L22 mm) assisted	
Top view	Side view	Top view	Side view
			
(A) During reaction		(D) During reaction	
			
(B) Before reaction	(C) Reactor wall	(E) Before reaction	(F) Reactor wall

Note: Reforming mode: POX-CH₄, Feeding rate: 10 NLmin⁻¹, O₂/CH₄ = 1, Catalyst: Pt-Rh base (Monolith). Temperature location: Upstream = T1, Middle-Stream = T2, Downstream = T3. Temperature distribution of catalyst without PM assisted: T1 = 930 °C, T2 = 860 °C, T3 = 851 °C. Temperature distribution of catalyst with PM assisted: T1 = 1127 °C, T2 = 1083 °C, T3 = 1018 °C.

temperature. Overall, the trend can be broadly divided into two categories: one which consists of an internal flow field with a PM, and the other without. Equilibrium adiabatic and reformate gas temperatures have a highly linear relationship, with reformate gas temperature ranging between 600 and 1100 °C.

For those reactions in which a PM was installed in the internal flow field, their overall reaction temperatures not only effectively were improved, but could be higher than those of the equilibrium adiabatic temperatures. It confirmed the view that PM can achieve the excess enthalpy on a reforming reaction. However, the temperature curve also shows that the material of PM has made a little difference in the reformate gas temperature. Regarding those reactions which did not include a PM in the internal flow field, the reformate gas temperatures were lower than the equilibrium adiabatic temperature.

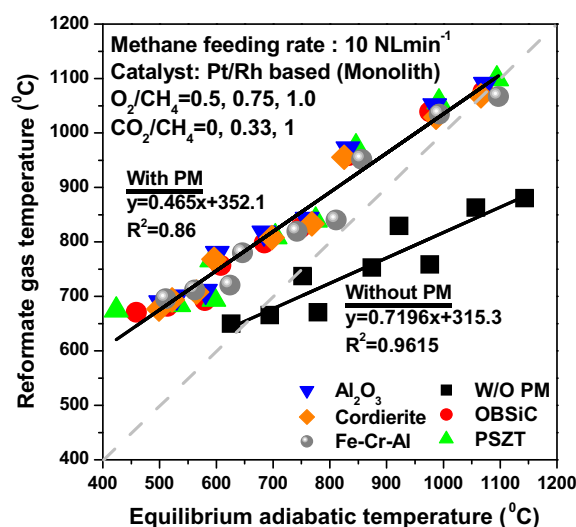


Fig. 5. Comparison of the equilibrium adiabatic temperature and reformate gas temperature under varying reforming parameters.

Fig. 6 shows the difference in temperatures of reformate gases with or without the addition of porous media to the internal flow fields. Through the selection of parameter settings and PM, when the O₂/CH₄ molar ratio is 1, the range of average gas temperature increased by 121–218 °C; when the O₂/CH₄ molar ratio is 0.75, the range of average gas temperature increased by between 19 and 81 °C; and when the O₂/CH₄ molar ratio is 0.5, the range of average gas temperature increased by 16–50 °C. These results indicate that the higher the O₂/CH₄ molar ratio, the more significant increase in the overall temperature was obtained.

Next, the temperature distribution at various positions in the upstream, mid-stream, and downstream sections of the catalyst zone was investigated. The previously collected data indicated that under different materials of PM, the differences in temperatures followed a consistent pattern. The gas temperature distribution with OBSiC made medium, which has a high thermal diffusivity,

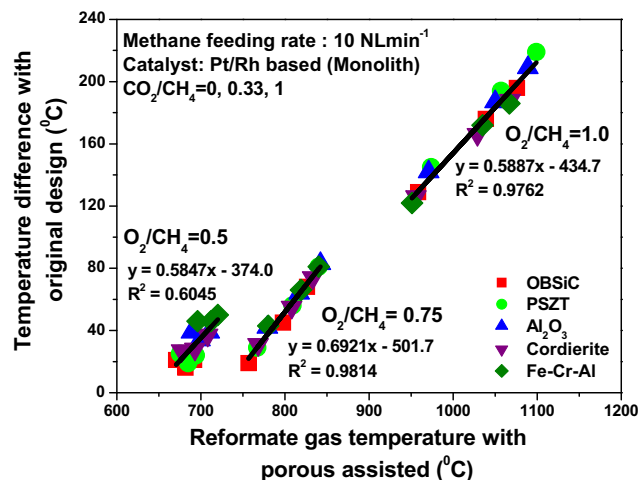


Fig. 6. Comparison of the reformate gas temperature and temperature gradient under varying reforming parameters.

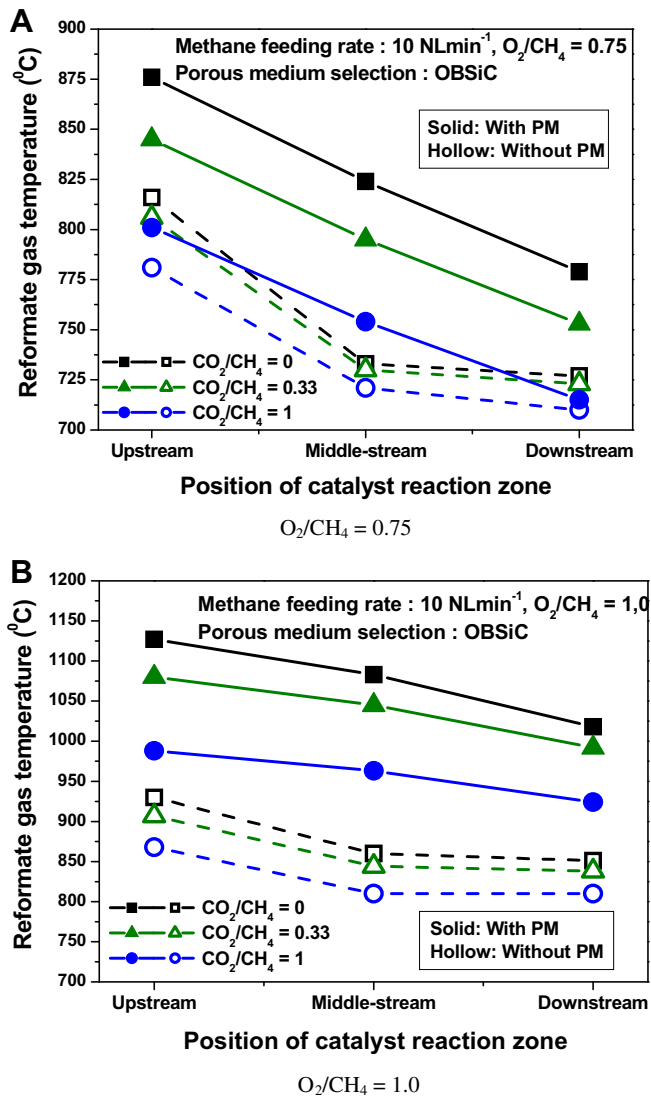


Fig. 7. Reformate gas temperature at different position of catalyst under various O₂/CH₄ molar ratio.

was further investigated. Fig. 7(A) and (B) shows the relationship of reformate gas temperature distribution under the well regulated feeding ratio, with the O₂/CH₄ molar ratio at 0.75 and 1.0, and the CO₂/CH₄ ratio set between 0 and 1. This experiment was designed to carry out autothermal reforming, which included partial oxidation reforming and carbon dioxide reduction reactions. Partial oxidation had a comparatively higher equilibrium constant, and the oxidation reaction easily occurred at the upstream catalyst, creating a certain catalyst bed temperature gradient. The reformate gas temperatures were measured at the upstream, mid-stream, and downstream positions of the catalyst. The experimental results show that when the internal flow field is configured with a PM (OBSiC), the temperatures of the upstream, mid-stream, and downstream of the catalyst are not only higher than those without the PM, they are also able to increase the reaction gas temperature at the mid-stream section of the catalyst. In the autothermal reforming reaction, high CO₂/CH₄ ratio also reduced the reformate gas temperature. The higher reforming reaction temperature of those assisted by PM was also discovered to benefit from a reverse water gas shifting reaction. Therefore, CO₂/CH₄ ratio allocation generated a larger temperature gradient.

4.2. Effect of porous media assisted DATR on performance index of reforming process

Next, the effect of PM on the reforming performance index of the dry autothermal reforming will be explored. Fig. 8 shows the effect of the reformate gas temperature on the methane conversion efficiency under the well regulated feeding ratios and PM. The theoretical calculation of chemical equilibrium demonstrated that the higher reaction temperature can give the better conversion of methane, as shown in Fig. 4(C). Therefore, the improvement in methane conversion efficiency can be attained with a higher O₂/CH₄ molar ratio. Under the experimented parameters, methane conversion efficiency can be roughly divided into three areas based on O₂/CH₄ molar ratio settings. When the O₂/CH₄ ratio reached 0.75, it was in a period of growth exhibiting a significant increase in the methane conversion efficiency. By the time the O₂/CH₄ ratio reached 1.0, it was almost completely converted. Therefore, methane conversion efficiency is clearly related to reformate gas temperature, and reformate gas temperature is related to feeding ratio and the material of the PM. Therefore, it can be confirmed that PM-assisted excess enthalpy in the internal flow field of the reforming reaction not only can improve the reformate gas temperature, it can also significantly increase methane conversion efficiency.

Fig. 9 shows the relationship of energy loss to reforming efficiency and unconverted methane molar fraction in products, relative to the placement of porous medium in the internal flow field. Here, the total energy loss consisted of sensible heat energy loss carried away by the products during the oxidation process, and losses due to reactor wall heat dissipation. The results demonstrated that the energy loss was in the range of 8–31%, which was defined in Eq. (6). The reforming efficiency is determined by the ratio between the reactant and the product heating values in the reforming reaction, and the highest value measured was 74%. The reforming efficiency is defined by Eq. (7). Overall, those reactions with a PM installed in the internal flow fields were able to attain a better reforming efficiency and reduced energy loss percentage. These improvements were achieved due to an increase in the reformate gas temperature under excess enthalpy, which exceeded the equilibrium adiabatic temperature. This allowed the methane conversion efficiency to improve effectively, increasing the production of hydrogen and carbon monoxide. However, in the autothermal reforming process, both of the reforming efficiency

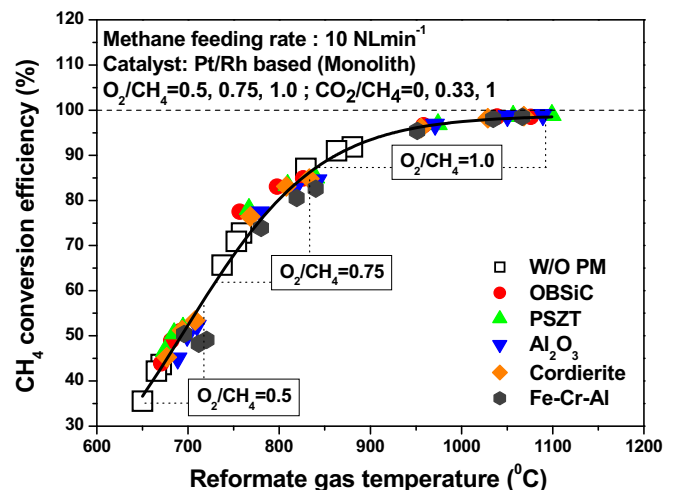


Fig. 8. Reformate gas temperature on methane conversion efficiency under varying reforming parameters.

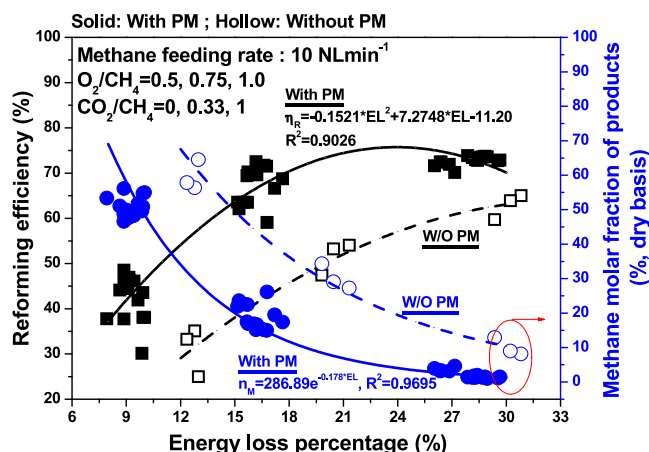


Fig. 9. Relationship between energy loss percentage, methane molar fraction of products and reforming efficiency under varying reforming parameters.

and the energy loss percentage must be considered simultaneously, and the necessary tradeoff in the selection of parameters was to be found. In this study, it revealed that the setting of O_2/CH_4 molar ratio at 0.75 could achieve a better reforming efficiency and a relatively low energy loss.

Table 4 shows the installation of PM on the reforming performance index, in which non-porous medium (W/O PM), and with the PM made of OBSiC, PSZT, Al_2O_3 , Cordierite, and Fe–Cr–Al were separately explored. The reforming performance included catalyst reaction temperature, molar fraction of products, methane conversion efficiency, syngas concentration, hydrogen and carbon monoxide selectivity, equilibrium adiabatic temperature, reforming efficiency, thermal efficiency, energy loss, and enthalpy of reaction. Among them, thermal efficiency was calculated using Eq. (8). Overall, PMs were favorable to improve the catalyst reaction temperature, especially Al_2O_3 and Fe–Cr–Al. However, in terms of molar fraction for products and reforming performance indicators, ceramic materials (OBSiC, PSZT and Al_2O_3) are similar to each other. Though Fe–Cr–Al was able to raise its reaction temperature, its improvement in reforming performance was insignificant. Although PMs did not participate in any chemical reactions during the reforming reaction, the reforming performance was affected by the variations in thermal properties and geometry of PMs. From the perspective of thermal properties, OBSiC media possess the

characteristic of high thermal diffusivity, which is suitable for preheating and improving the convection heat transfer between solid and gas interface. Zirconia oxide media have a good thermal resistance, but low heat capacity and conductivity. Alumina oxide media are high heat capacity materials that are most commonly used to preheat reactants within the internal flow field, but which include the disadvantages of a high coefficient of thermal expansion and a small thermal shock resistance [29]. The open areas of cellular media in cordierite and Fe–Cr–Al are much larger than those in the ceramic foam. The reforming effectiveness of honeycomb monolith was rather poor, which may be due to the channeling effect within the honeycomb geometry. The gas was not able to mix thoroughly within the limited space, resulting in poor convection heat transfer. Thus, PMs with a small pore structure were recommended for future applications. The process also revealed that OBSiC medium can be used to improve the overall conversion effects, and its reformat gas temperature is the lowest among all the tested materials. Perhaps due to its excellent convective heat transfer effect, OBSiC medium has led to occurrence of reductions at the upstream catalyst, such that the temperature at the upstream section of the catalyst reaction was decreased. Next, the performance index of the reforming reaction with OBSiC will be discussed.

Fig. 10 shows the effect of reformat gas temperature on the produced gas concentration and the enthalpy of reaction. The parameters for reforming were set as the methane flow rate at 10 NLmin^{-1} , $CO_2/CH_4 = 1$ and $O_2/CH_4 = 0.75$. $CO_2/CH_4 = 1$ is the best ratio for syngas production according to the theoretical calculation for dry reforming; $O_2/CH_4 = 0.75$ is the best parameter found in this experiment, and the best reforming efficiency and lower energy loss were achieved. Fig. 10 shows the comparison of values generated from the theoretical calculation of chemical equilibrium with experimental values. The theoretical calculation of chemical equilibrium used the minimization of Gibbs free energy to predict various hydrogen-rich gas molar fractions generated by the reforming process, which are authenticated by experimental results. Based on the setting of the experimented parameters, the reformat gas temperature was similar to that generated by the theoretical calculation of the chemical equilibrium. Though the reformat gas temperature under excess enthalpy with PM assisting increased, little difference was made to the concentration of the produced gases. Theoretical calculations also indicated that hydrogen and carbon dioxide will generate reverse water gas shifting reaction under high temperature condition, which also

Table 4
Effect of the PM on performance index.

	W/O PM	OBSiC	PSZT	Al_2O_3	Cordierite	FeCrAl
Temperature of catalyst upstream ($^{\circ}\text{C}$)	781	801	815	834	818	833
Temperature of catalyst stream ($^{\circ}\text{C}$)	721	754	764	775	761	779
Temperature of catalyst downstream ($^{\circ}\text{C}$)	710	715	721	728	726	728
Molar fraction of products (N_2 Bal.)						
H_2	0.132	0.180	0.180	0.179	0.172	0.166
CO	0.105	0.128	0.128	0.128	0.130	0.122
CO_2	0.168	0.155	0.153	0.154	0.150	0.158
CH_4	0.056	0.035	0.034	0.035	0.037	0.041
H_2O	0.081	0.062	0.064	0.063	0.068	0.067
CH_4 conversion efficiency (%)	65.65	77.50	78.03	77.39	76.43	73.90
Syngas concentration (%)	25.85	32.79	32.92	32.81	32.37	30.92
H_2 selectivity (%)	61.95	74.31	73.79	73.97	71.62	71.31
CO selectivity (%)	98.94	105.27	104.60	106.07	107.78	104.54
Equilibrium adiabatic temperature ($^{\circ}\text{C}$)	752	608	592	602	596	646
Reforming efficiency (%)	47.46	63.54	63.55	63.51	62.09	59.06
Thermal efficiency (%)	81.81	86.04	85.52	86.12	85.66	85.16
Energy loss percentage (%)	19.81	15.70	15.06	15.48	15.23	16.78
Enthalpy of reaction ($\text{kJ}/(0.405 \text{ mole-CH}_4)^{-1}$)	−64.0	−50.7	−49.0	−50.0	−49.2	−54.2

Note: $CO_2/CH_4 = 1$, $O_2/CH_4 = 0.75$, CH_4 feeding rate = 10 NLmin^{-1} , Catalyst selection = Pt/Rh based (Monolith).

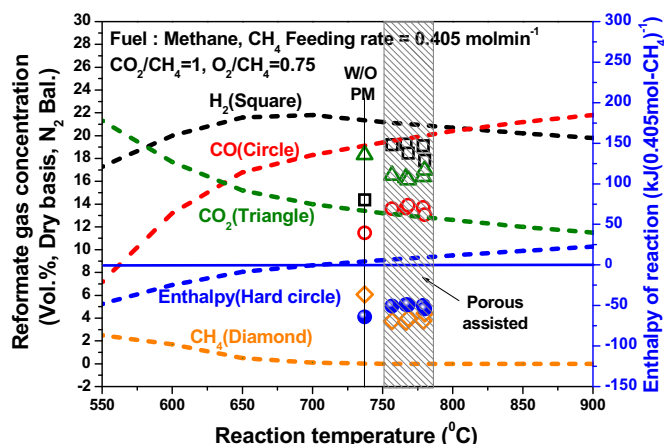


Fig. 10. Reaction temperature on reformat gas concentration and enthalpy of reaction with or without porous media.

promoted the transfer of carbon dioxide into carbon monoxide. The theoretical values are fairly consistent with the experimental results. Due to excess enthalpy reaction, the enthalpy from the experimental value was slightly lower than the theoretical prediction.

Fig. 11 shows the improvement in the reforming performance index of OBSiC media assisted dry autothermal reforming. A number of performance indices could be referred for the reforming, which depend on the field of application. Among them, the most important reforming performance indicators are reforming efficiency, energy loss percentage, selectivity, and conversion efficiency. As shown in Fig. 11, the reforming performance indices could be raised under the excess enthalpy reaction with the installation of PM in the flow field. Though the increase of the calculated average temperature of the reformat gas was only by 2.6%, the improvement of methane conversion efficiency was by 18%, carbon monoxide selectivity by 6.4%, hydrogen selectivity by 20%, reforming efficiency up to 33.9%, and energy loss percentage by 20.7%. These results confirmed that dry autothermal reforming reaction does not require additional energy, but instead use their own internal heat recirculation from oxidation to improve the reforming performance indices.

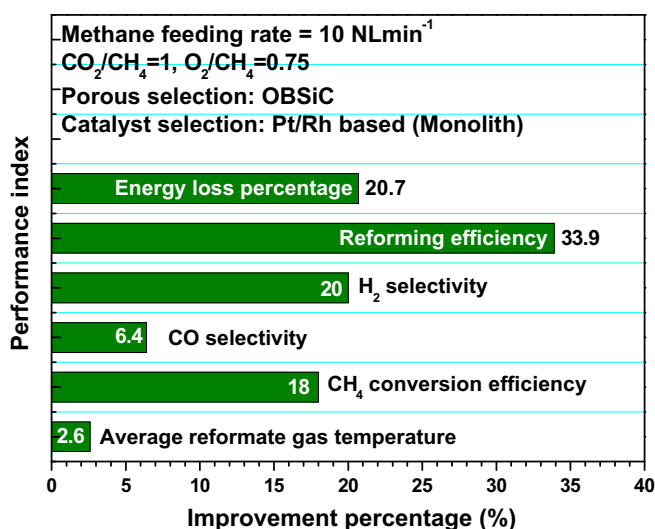


Fig. 11. Improvement percentage of reforming performance index under porous media (OBSiC foam) assisted dry autothermal reforming.

5. Conclusions

Hydrogen-rich syngas production by dry autothermal reforming from BDG with porous media under excess enthalpy was investigated in this study. The reforming parameters included methane feeding rate, CO_2/CH_4 molar ratio, O_2/CH_4 molar ratio, and porous medium material. Hydrogen-rich syngas production performance and reaction temperature were investigated by performing a series of experiments. The conclusions of the experimental results were obtained, as follows:

1. Based on the fire observation and reaction temperature measurement, the reaction temperature of the catalyst bed and the heat loss were improved by the porous media adoption. Therefore, the porous media arrangement may have been helpful in preheating the reactant by heat recirculation. It could contribute to the uniformity of gas distribution to decrease the gradients of temperature and concentration in the reaction chamber.
2. The reformat gas temperature of the dry autothermal reforming could be increased with the assistance of a porous medium, possibly higher than the equilibrium adiabatic temperature. The results indicated that the reformat gas temperature varied with equilibrium adiabatic temperature in a linear relationship. Additionally, the apparent improvement of temperature increase in the porous medium was accompanied by higher reformat gas temperature; therefore, the temperature of the catalyst reaction zone increased substantially. Consequently, the provision of external energy to the dry autothermal reforming was not required for a self-sustaining reaction, although it is a strongly endothermic reaction.
3. The experimental results indicated that the thermo-physical properties and geometry could affect reformat gas concentration. OBSiC media exhibit characteristics of high thermal diffusivity, and it implied that it increased convection heat transfer between the solid and gas interface in the preheating zone. Therefore, better syngas production was achieved under relatively low catalyst reaction temperature. In addition, the honeycomb structure with a higher opening ratio constrained the benefit of internal heat recirculation because of the channeling effect. Therefore, use of a small pore structure of porous medium is recommended for the preheating zone.
4. Reforming performance improvement was achieved on dry autothermal reforming with porous media assisting. The improvement in methane conversion efficiency was 18%, CO selectivity was 6.4%, H_2 selectivity was 20%, reforming efficiency was 33.9%, and energy loss percentage was 20.7%, respectively under the excess enthalpy reforming reaction with the best parameter settings ($\text{CO}_2/\text{CH}_4 = 1$ and $\text{O}_2/\text{CH}_4 = 0.75$) by the OBSiC porous medium.

Acknowledgements

The authors are grateful to the support of the National Science Council of Taiwan under grant number NSC 100-2221-E-168-038-MY2.

References

- [1] X. Hao, H. Yang, G. Zhang, Energy Policy 36 (2008) 3662–3673.
- [2] J. Bekkering, A.A. Broekhuis, W.J.T. van Gemert, Bioresource Technol. 101 (2010) 450–456.
- [3] C. Liu, B. Yan, G. Chen, X.S. Bai, Int. J. Hydrogen Energy 35 (2010) 542–555.
- [4] R.F. Horng, C.S. Wen, C.T. Liauh, Y. Chao, C.T. Huang, Int. J. Hydrogen Energy 33 (2008) 7619–7629.
- [5] A. Tsolakis, A. Megaritis, Biomass Bioenergy 27 (2004) 493–505.
- [6] Y. Shiratori, T. Oshima, K. Sasaki, Int. J. Hydrogen Energy 33 (2008) 6316–6321.

- [7] C.S. Song, W. Pan, Catal. Today 98 (2004) 463–484.
- [8] V. Havran, M.P. Dudukovi, C.S. Lo, Ind. Eng. Chem. Res. 50 (2011) 7089–7100.
- [9] F. Fischer, H. Tropsch, Brennst. Chem. 3 (1928) 39.
- [10] A.T. Ashcroft, A.K. Cheetham, M.L.H. Green, P.D.F. Vernon, Nature 352 (1991) 225–226.
- [11] E. Ruckenstein, Y.H. Hu, Appl. Catal. A Gen. 133 (1995) 149–161.
- [12] T. Horiuchi, K. Sakuma, T. Fukui, Y. Kubo, T. Osaki, T. Mori, Appl. Catal. A Gen. 144 (1996) 111–120.
- [13] Z. Hou, P. Chen, H. Fang, X. Zheng, T. Yashima, Int. J. Hydrogen Energy 31 (2006) 555–561.
- [14] A.M. O'Connor, F.C. Meunier, J.R.H. Ross, Stud. Surf. Sci. Catal. 119 (1998) 819–824.
- [15] A.M. O'Connor, J.R.H. Ross, Catal. Today 46 (1998) 203–210.
- [16] Q. Jing, H. Lou, L. Mo, X. Zheng, Energy Convers. Manage. 47 (2006) 459–469.
- [17] F.J. Weinberg, Nature 233 (1971) 239–241.
- [18] A.K. Gupta, J. Eng. Gas Turb. Power 126 (2004) 9–19.
- [19] S.A. Lloyd, F.J. Weinberg, Nature 257 (1975) 367–370.
- [20] K. Kitagawa, N. Konishi, N. Arai, A.K. Gupta, in: Proc. ASME Int. Jt. Power Gener. Conf. (IJPGC), ASME Fact, vol. 22, 1998, pp. 239–242.
- [21] T.L. Marbach, A.K. Agrawal, J. Eng. Gas Turb. Power 127 (2005) 307–313.
- [22] H. Pedersen-Mjaanes, L. Chan, E. Mastorakos, Int. J. Hydrogen Energy 30 (2005) 579–592.
- [23] A. Pastore, E. Mastorakos, Fuel 90 (2011) 64–76.
- [24] Z. Al-Hamamre, S. Diezinger, P. Talukdar, F. Von Issendorff, D. Trimis, Process Saf. Environ. 84 (2006) 297–308.
- [25] Z. Al-Hamamre, S. Voß, D. Trimis, Int. J. Hydrogen Energy 34 (2009) 827–832.
- [26] G.W. Hallum, T.P. Herbell, in: Eighty Eighth Annual Meeting of the American Ceramic Society, Chicago, Illinois (1986).
- [27] A.A.M. Oliveira, M. Kaviany, Prog. Energ. Combust. Sci. 27 (2001) 523–545.
- [28] HSC Chemistry. Version 5.11, Outokumpu Research Oy, Pori, Finland, 2002.
- [29] C. Tierney, A.T. Harris, J. Aust. Ceram. Soc. 45 (2009) 20–29.